

(12) UK Patent Application (19) GB (11) 2 274 197 (13) A

(43) Date of A Publication 13.07.1994

(21) Application No 9300406.7

(22) Date of Filing 11.01.1993

(71) Applicant(s)

Kratos Analytical Limited

(Incorporated in the United Kingdom)

Barton Dock Road, Urmston, MANCHESTER,
M31 2LD, United Kingdom

(72) Inventor(s)

Stephen Charles Davis

Alexander Alekseevich Makarov

(74) Agent and/or Address for Service

Mathisen Macara & Co

The Coach House, 6-8 Swakeleys Road, Ickenham,
UXBRIDGE, Middlesex, UB10 8BZ, United Kingdom

(51) INT CL⁵

H01J 49/40 49/06 49/22

(52) UK CL (Edition M)

H1D DMAA D21A D21B D21X

(56) Documents Cited

GB 1448322 A

GB 1326279 A

EP 0456517 A2

EP 0456516 A2

EP 0408288 A1

WO 91/03071 A1

WO 89/06044 A1

(58) Field of Search

UK CL (Edition L) H1D DMAA DMC DMD DME DMF

INT CL⁵ H01J

(54) Time-of-flight mass spectrometer

(57) A time-of-flight mass spectrometer has an ion-extraction device (30) for accelerating a section (S) of an ion beam (B) transversely with respect to the direction of the beam path, and in the arrangement shown, an ion mirror (40) in the form of a monopole electrode structure, for example, Figs 2 and 3 (not shown), is used to bring the ions in the accelerated section of the beam to a focus, with respect to both time and space, at detector 60. Alternatively, Fig. 4 (not shown), the transversely accelerated section of the ion beam may be focussed by an acceleration lens (70) defining an electrostatic quadrupole field through drift tube 50 to the detector 60. In another arrangement, Figs. 5 and 6 (not shown), the extractor device 30 comprises divergent deflector plates which are effective to modify the ion energy in the beam section S as a function of position along the beam path, the transversely accelerated ions being brought to a focus with the aid of a further deflecting field between plates (80, 80'). In a further arrangement the ion energy is modified in an ion buncher, Figs. 7 and 8 (not shown), prior to their transverse acceleration from the beam path Y-Y.

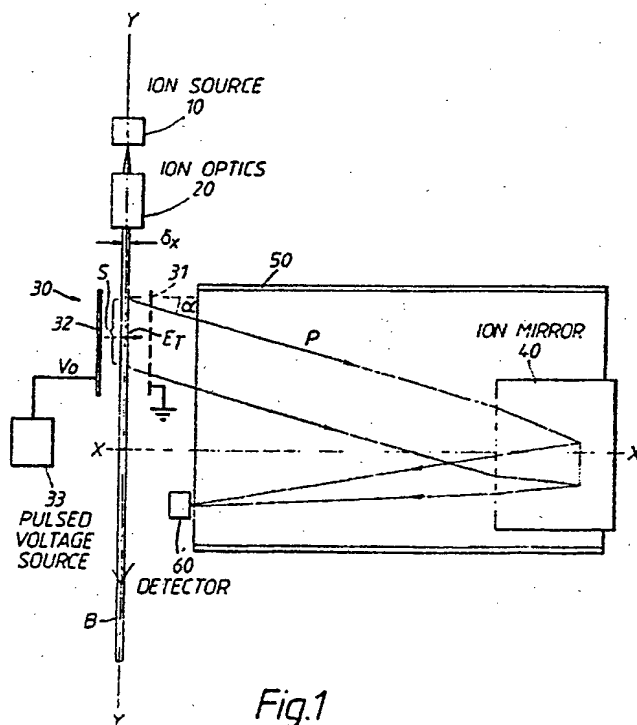


Fig.1

1/4

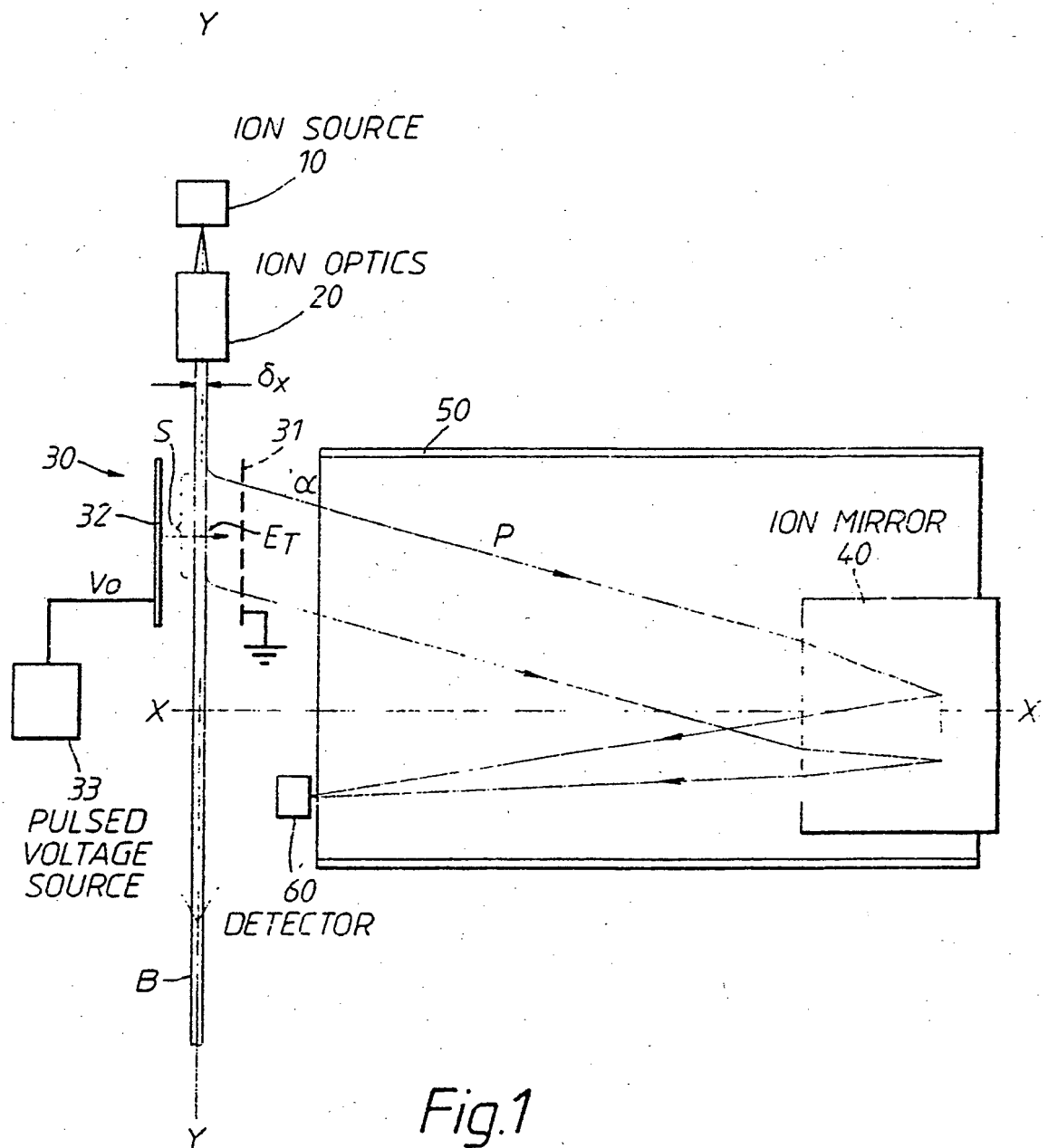
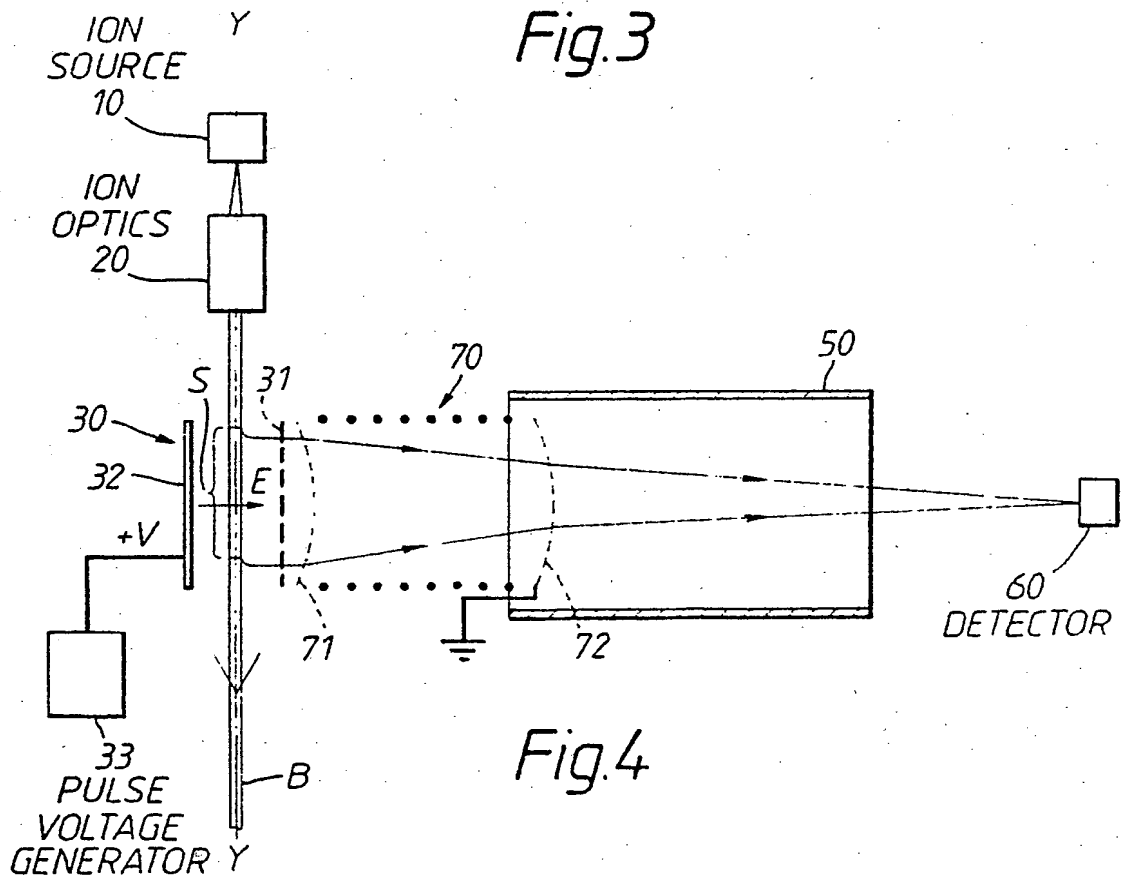
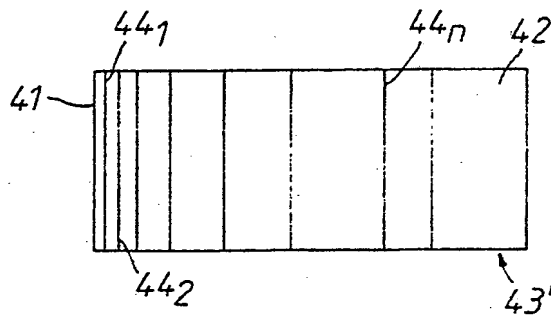
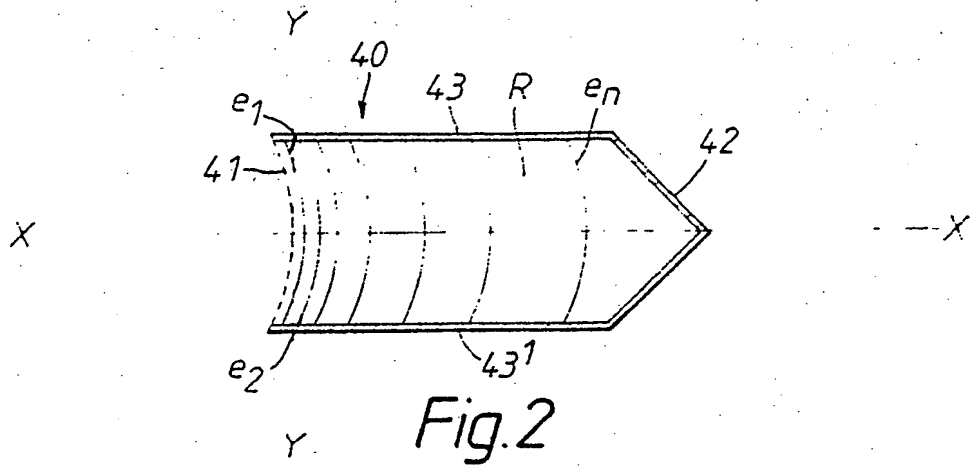


Fig.1

2/4



3/4

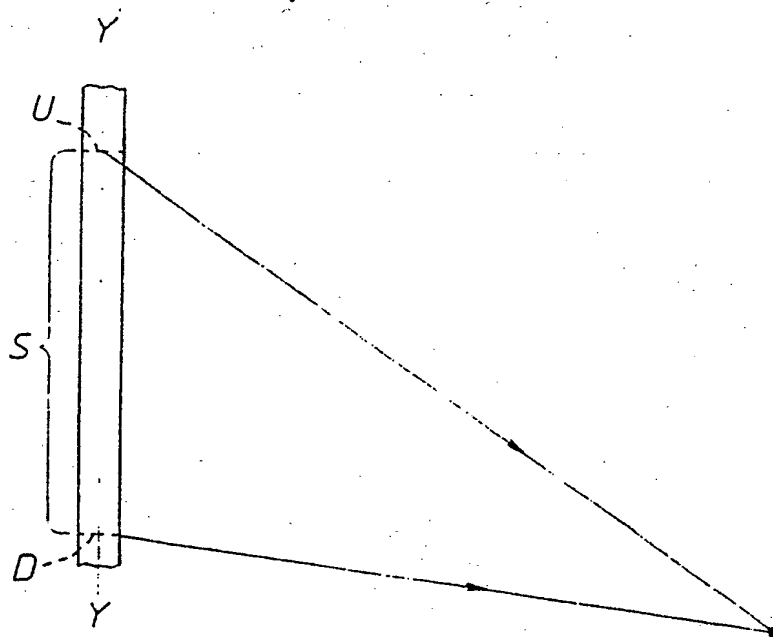


Fig. 5

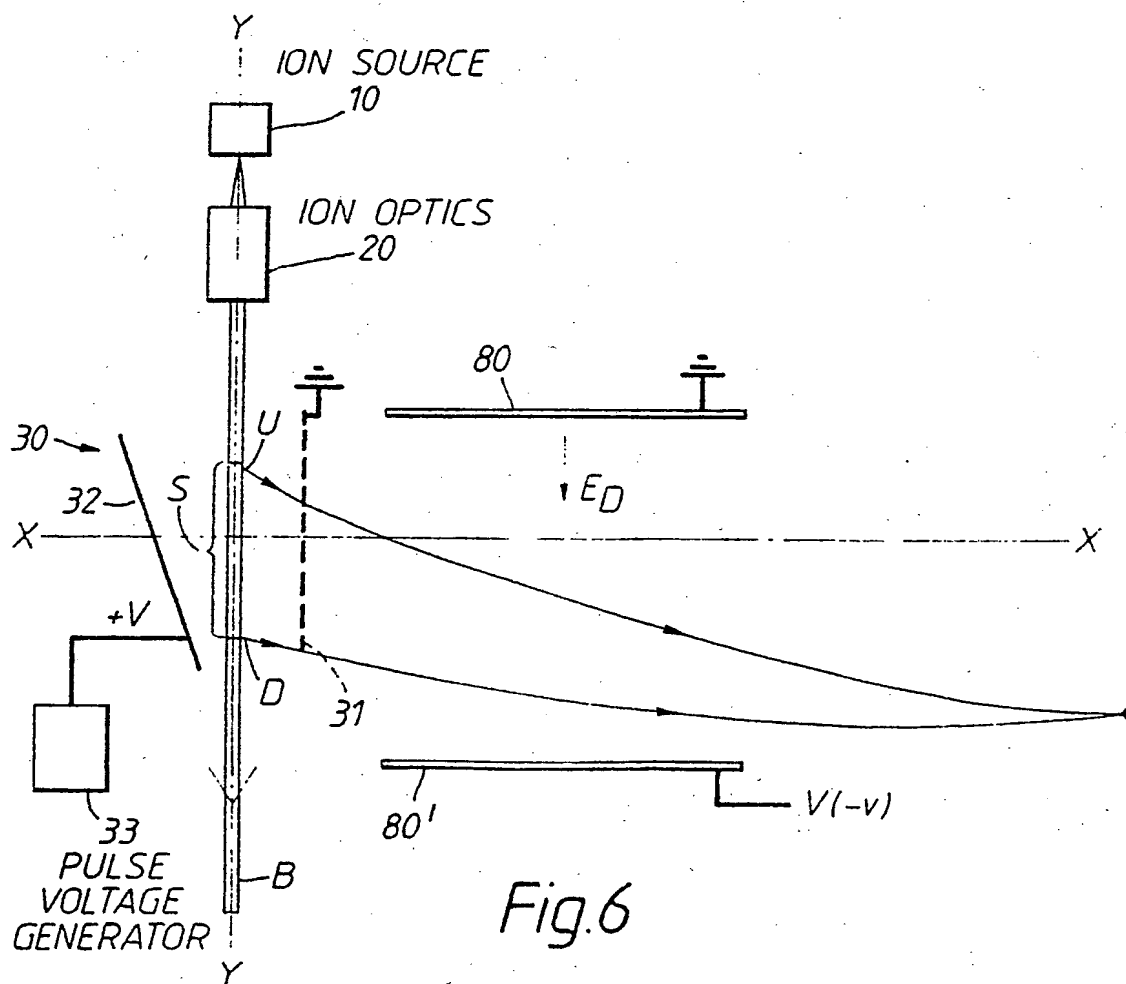
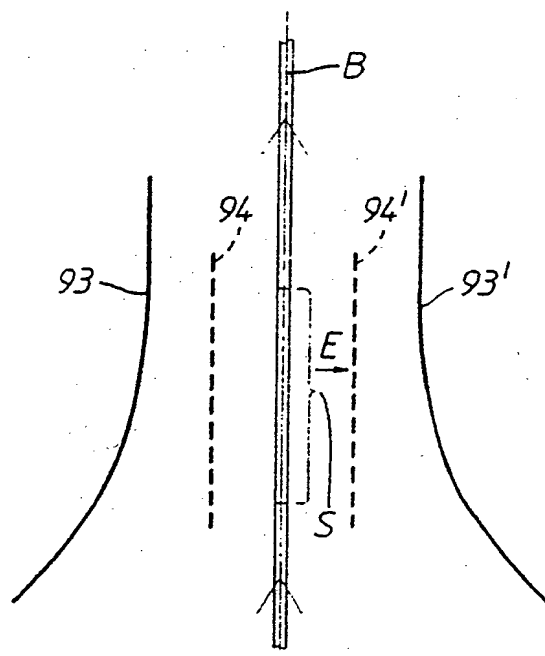
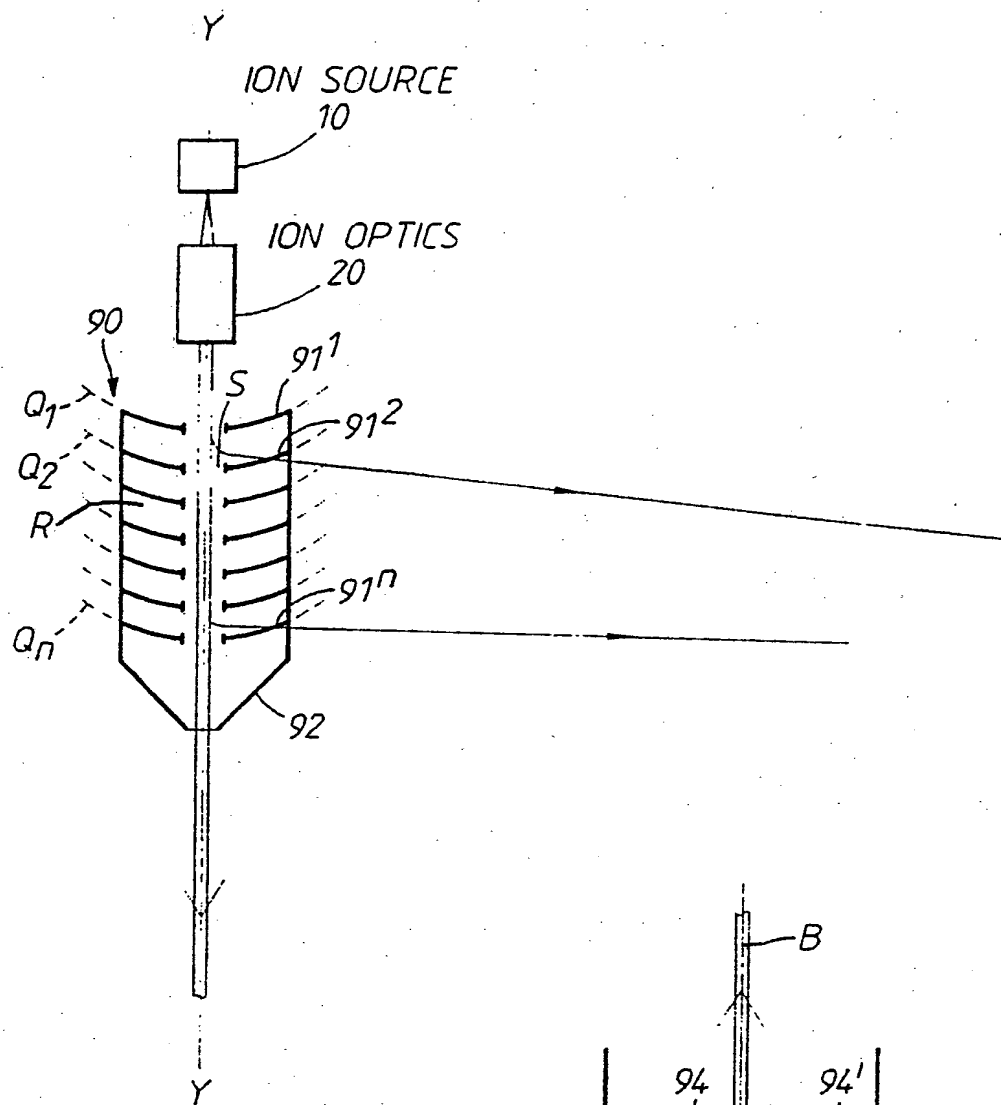


Fig. 6



TIME-OF-FLIGHT MASS SPECTROMETER

This invention relates to time-of-flight (TOF) mass spectrometers, particularly, though not exclusively, TOF mass spectrometers having continuous beam ion sources.

One of the earliest techniques used to derive ion pulses from a continuous beam of ions involved passing the beam between a pair of deflector plates.

For the majority of the time, the deflector plates are energised to deflect the ion beam away from the mass analyser; however, periodically, the deflector plates are de-energised, for a short time interval Δt , allowing a short pulse of ions to pass to the mass analyser.

The mass resolution R of the analyser is given by the expression $R = t/2\Delta t$, where t is the total flight time of the ions through the analyser. Therefore, to achieve high resolution, Δt needs to be as small as possible, and so most of the beam is deflected away from the analyser i.e. the duty cycle is very low.

In an article by D.W. Thomas in Proc. of 1st. European Symposium on TOF Mass Spectrometry, p.171-210, Pergamon Press 1969, there is described an ion source for use in a

TOF mass spectrometer. In this system, a section of ion beam is accelerated transversely with respect to the direction of the beam path and is thereby extracted from the beam for analysis. The longer the section of beam extracted, the higher the duty cycle; however, in the described arrangement, longer extracted beam sections require larger detectors, and this constraint limits the usefulness of the technique. Furthermore, the performance of this method is dependent on how parallel the beam can be made prior to extraction.

It is an object of the invention to provide a time-of-flight mass spectrometer which substantially alleviates the afore-mentioned problems.

According to one aspect of the invention, there is provided a time-of-flight mass spectrometer comprising, an ion source; beam-forming means for producing a beam of ions generated by the ion source, the beam of ions extending along a path; an extraction means for accelerating a section of the beam transversely with respect to the direction of the path; focussing means for bringing ions in the accelerated section of beam, having the same mass-to-charge ratio, to a focus with respect to both time and space, and means for detecting the ions focussed by the focussing means.

According to another aspect of the invention there is provided a time-of-flight mass spectrometer comprising an ion source, beam-forming means for producing a beam of ions generated by the ion source, the beam of ions extending along a path, extraction means for accelerating a section of the beam transversely with respect to the direction of the beam path, focussing means for focussing ions in the accelerated section of beam, which have the same mass-to-charge ratio, with respect to both time and space, and means for detecting the ions focussed by the focussing means, wherein the focussing means comprises modifying means for modifying the component of ion energy in the direction of the beam path as a function of position along said section of beam prior to said section of beam being accelerated transversely with respect to the direction of the beam path.

According to a yet further aspect of the invention, there is provided a time-of-flight mass spectrometer comprising, an ion source, beam-forming means for producing a beam of ions generated by the ion source, the beam of ions extending along a path, an extraction means for accelerating a section of the beam transversely with respect to the direction of the path, focussing means for bringing ions in the accelerated section of beam, having the same mass-to-charge ratio, to a focus with respect to

both time and space, and means for detecting the ions focussed by the focussing means, wherein the extraction means is effective to modify ion energy as a function of position along the beam path.

Embodiments of the invention are now described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 shows one embodiment of the invention;

Figure 2 is a transverse cross-sectional view through an ion mirror used in the embodiment of Figure 1;

Figure 3 is a side view of the ion mirror;

Figure 4 shows another embodiment of the invention;

Figure 5 illustrates how spatial focussing can be accomplished by modifying the energies of ions;

Figure 6 illustrates a further embodiment of the invention;

Figure 7 illustrates a yet further embodiment of the invention employing an ion buncher; and

Figure 8 shows a modification of the embodiment shown in Figure 7.

Referring now to Figure 1, the illustrated time-of-flight (TOF) mass spectrometer comprises an ion source 10, ion optics 20, an ion-extraction device 30, an ion mirror 40 housed within a flight tube 50 and a detector 60, these components being contained within a continuously pumped, high vacuum envelope (not shown in the drawings).

The ion source 10 operates in continuous mode and may be of conventional form; for example, electron or ion impact, thermospray, electrospray and fast atom bombardment (FAB) sources could be used, and such sources may have conventional inlet systems as employed, for example, in liquid or gas chromatography mass spectrometry or in other continuous flow systems.

Ions generated by ion source 10 are formed into a narrow, substantially parallel beam B by the ion optics 20.

The beam extends along a path in the Y-axis direction and passes through the ion-extraction device 30. As will be described, the function of the ion-extraction device is to accelerate a section S of the beam in the transverse (X-axis) direction to extract that section of beam for

subsequent analysis. To that end, the ion-extraction device 30 comprises two, parallel electrodes 31,32 disposed to either side of beam B. Electrode 31 is a grid or slit electrode which is maintained at earth potential, whereas electrode 32 is a plate electrode which is pulsed to a suitable d.c. voltage V_0 using a pulsed voltage source 33 whereby to initiate sideways acceleration of the beam section S.

Between successive voltage pulses, electrode plate 32 is maintained at earth potential thereby creating a field-free region between the electrodes. In this mode of operation, beam B passes straight through the ion-extraction device 30 without being deflected. However, when electrode plate 32 is pulsed to voltage V_0 , a transverse electric field E_T is generated between electrodes 31,32, causing the beam section S to be accelerated sideways. In this way, section S is extracted from the beam and is projected through the grid electrode 31 into flight tube 50.

The ions in section S will still have a component of velocity in the Y-axis direction and will therefore move along a path P which is inclined at a shallow angle α to the transverse (X-axis) direction.

Beam B has a finite width δx and so ions in section S which are relatively close to electrode plate 32 will experience an accelerating field for longer when the electrode is pulsed to voltage V_0 than ions having the same mass-to-charge ratio that are closer to the grid electrode 31. Accordingly, ions which have the same mass-to-charge ratio will, nevertheless, be accelerated to different velocities depending on their relative positions (in the X-axis direction) in the beam. This effect can be corrected for by the present arrangement.

The extracted beam section S enters ion mirror 40 which focusses the ions with respect to both space and time.

The ion mirror defines a non-uniform field region which is effective to focus the beam section in thickness (i.e. in the direction of travel) and in width (i.e. in the direction orthogonal to the direction of travel). The effect of compressing the beam section in the direction of travel is substantially to eliminate timing errors at detector 60, whereas compression in the orthogonal direction enables a wider beam section to be extracted and analysed without the need for a larger detector, thereby improving the duty cycle of the ion-extraction device.

The optimum aspect ratio of beam width (i.e. in the Y axis

direction) to ion mirror width can be accomplished using an ion mirror defining an electrostatic quadrupole field having two-dimensional symmetry about the X-axis. An electrode structure of a form suitable to generate a field of this kind is a monopole electrode structure. Referring to Figure 2, the monopole electrode structure comprises two elongate electrodes 41,42 which are spaced apart from each other along the X-axis and are disposed symmetrically about the X-Z plane. Electrode 41 is a grid electrode or slit having a circular or hyperbolic transverse cross-section, whereas electrode 42 has a substantially V-shaped transverse cross-section, subtending an angle of 90° and is maintained at a d.c. retarding voltage with respect to electrode 41.

The electrostatic quadrupole field generated in the field region R between electrodes 41,42 is defined by equipotential surfaces which extend parallel to the Z-axis and are hyperbolic in the X-Y plane, as exemplified by the equipotential field lines $e_1, e_2 \dots e_n$ shown in Figure 2. The electrode structure has parallel side walls 43,43' made from an electrically insulating material and these may be provided with discrete parallel electrodes $44_1, 44_2, \dots 44_n$, as shown in the side view of Figure 3. Each such electrode $44_1, 44_2 \dots 44_n$ lies on the line of intersection with a respective

equipotential surface and is maintained at a corresponding retarding voltage.

The electrode structure may also have end walls (not shown) and these may also bear discrete electrodes, each lying on a hyperbolic line of intersection.

The extracted beam section enters field region R through the grid electrode 41 and is compressed in width by the curvature of the field lines causing the reflected beam section to be brought to a spatial focus at the detector 60. Furthermore, for a given mass-to-charge ratio, relatively energetic ions in the beam section (i.e. those having the higher velocities) will penetrate deeper into field region R before being reflected and will arrive at the detector 60 at substantially the same time as less energetic ions which do not penetrate the field region to the same extent. In this way, ions which have the same mass-to-charge ratio are brought to a time focus at the detector thereby substantially eliminating timing errors i.e. compensates in analogous fashion to a standard reflectron.

Additional focussing (space and/or time) may be provided by a discrete lens or by setting the flight tube 50 at a different potential to that at the entrance to the ion

mirror, and the combined focussing actions can be suitably adjusted to attain the required time and spatial focus at the detector.

Figure 4 shows an alternative arrangement by which focussing with respect to both time and space can be accomplished. This arrangement includes an acceleration lens 70 which is positioned adjacent to the ion-extraction device 30 and has a focussing effect on the accelerated beam section S. As in the case of ion mirror 40, described with reference to Figures 2 and 3, the acceleration lens 70 has an electrode structure defining an electrostatic quadrupole field; however, in contrast to the ion mirror, the upstream and downstream electrodes 71,72 are both in the form of grid or slit electrodes to allow the beam section S to pass through the lens, and the upstream electrode 71 is set at a suitable voltage, a positive voltage for positive ions with respect to the downstream electrode 72 which, in this embodiment, is held at earth potential.

Beam section S passes through the acceleration lens 70 into flight tube 50 which may be held at a different potential relative to that at the downstream electrode 72 whereby to subject the beam section to additional focussing. A discrete lens may also be used. As before,

the combined focussing actions of the acceleration lens 70 and the drift tube 50 can be suitably adjusted to attain the required time and spatial focus at the detector.

If desired, further additional focussing may be provided using an ion mirror such as that referenced 40 in Figure 2 which would be positioned downstream of the acceleration lens 70.

In a yet further embodiment of the invention, the ion-extraction device 30 is effective to modify the energy of ions as a function of their position along the beam section S.

As illustrated in Figure 5, ions at the upstream end U of beam section S have a larger component of velocity in the Y-axis direction than ions at the downstream end D of the beam section. Accordingly, when the ions are subjected to a transverse accelerating force by the ion-extraction device 30 they will follow convergent trajectories, as exemplified in Figure 5 by the trajectories of ions at the upstream and downstream ends of the beam section, and are thereby brought to a spatial focus.

In a particular implementation, shown in Figure 6, the ion-extraction device 30 is arranged to subject beam

section S to a non-uniform, transverse electric field, and the accelerated beam section is passed through a pair of deflector plates 80,80' which subject the ions to an electrostatic deflection field E_D which is substantially orthogonal to the direction of travel of the beam section (downwardly in the drawing). In this arrangement, electrode plate 32 (which may be non-planar) of the ion extraction device 30 is inclined with respect to the grid electrode 31 such that ions at the downstream end of the beam section experience a stronger field gradient between electrodes 31,32 than ions at the upstream end, and will therefore have a greater component of velocity in the X-axis direction than ions having the same mass-to-charge ratio at the upstream end. Differences in flight times caused by this difference in velocities is compensated for by differences in flight times inside the plates 80,80'.

Accordingly, in this example, ions at the downstream end of the beam section will undergo a smaller (downwards) deflection between plates 80,80' on account of their steeper initial trajectories and the shorter time spent between the plates. As a result, ions having the same mass-to-charge ratio will follow convergent trajectories, and by a suitable choice of field gradients between electrodes 31,32 and deflector plates 80,80' the ions can be brought to a focus with respect to both time and space.

Figure 7 illustrates another embodiment of the invention. In this arrangement an ion buncher 90 is used to accumulate ions in section S before the ions are extracted from the beam, and to modify the Y-axis component of ion velocity as a function of position along the beam section.

The ion buncher defines an electrostatic retarding field in the form of a quadrupole field and, in this embodiment, comprises a monopole electrode structure of the kind described in our co-pending European Patent Application, Publication No. 456,516.

The monopole electrode structure may either have two or three dimensional symmetry, about the Y-axis and may, in the two-dimensional case, comprise an upstream electrode 91 having a curvilinear e.g. circular or hyperbolic transverse cross-section and a downstream electrode 92 having a substantially V-shaped transverse cross-section, subtending an angle of 90° , which is maintained at a suitable retarding voltage with respect to the upstream electrode 91. The upstream electrode 91 may be a grid electrode or alternatively a plate electrode having a central aperture by which the ion beam B can enter the field region R between the electrodes.

The electrostatic quadrupole field is defined by

equipotential surfaces $Q_1, Q_2 \dots Q_n$ which are hyperbolic in the X-Y plane. In the case of a quadrupole field having two-dimensional symmetry, the electrode structure may have electrically insulating side and end walls forming a box-like enclosure and, as in the case of ion mirror 40 described with reference to Figures 2 and 3, these may be provided with discrete electrodes each lying on the line of intersection with a respective equipotential surface and being maintained at a corresponding retarding voltage.

Alternatively, as described in the afore-mentioned copending European patent application, the upstream electrode 91 may be replaced by a plurality of such electrodes $91^1, 91^2 \dots 91^n$ spaced apart at intervals along the Y-axis, each electrode having a central aperture and conforming to a respective equipotential surface $Q_1, Q_2 \dots Q_n$. In the case of a quadrupole field having two-dimensioned symmetry, each electrode $91^1, 91^2 \dots 91^n$ would extend parallel to the Z-axis, whereas in the case of a quadrupole field having rotational symmetry, each electrode $91^1, 91^2 \dots 91^n$ would have the form of a hyperboloid.

Whatever the form of the electrode structure, beam section S is arranged to lie within the field region R of the ion

buncher. Ions entering the field region are progressively retarded as they travel along the beam path and this reduces their velocities in the Y-axis direction and causes ions to accumulate in the beam section. Accordingly, for a given mass-to-charge ratio, ions at the upstream end of the beam section (which are the most recent ions to have entered the ion buncher) will have a substantially higher velocity in the Y-axis direction than ions at the downstream end thereof. Therefore, when the beam section S is accelerated sideways, in the manner to be described, the ions of which it is comprised will follow convergent trajectories, as explained with reference to Figure 5, and will be brought to a spatial focus.

Section S may be extracted from the beam in a variety of different ways. For example, selected electrodes of the ion buncher corresponding to the defined section S may have a split configuration. Respective halves of the electrode may be disposed to either side of the beam path and would be energised to generate a transverse electric sweep field to accelerate beam section S sideways. With this arrangement, the ion buncher would operate alternately in two different modes; a "filling" mode in which the ion buncher generates the electrostatic quadrupole field to accumulate ions in beam section S and

modify their Y-axis direction velocities in the manner described, and an "extraction" mode in which the ion buncher operates as an ion-extraction device and is effective to uniformly accelerate the accumulated ions in the beam section in the transverse (X-axis) direction. The ion buncher 90 is, of course, provided with a suitable slit or aperture allowing the accelerated beam section to exit the buncher.

Alternatively, a separate ion-extraction device of the kind described with reference to Figure 1 could be provided in addition to ion buncher 90.

After extraction in the X-axis direction, the beam may be reflected through an ion mirror to provide additional energy focussing.

Figure 8 shows an alternative construction of the ion buncher. In this embodiment, the electrode structure described with reference to Figure 7 is replaced with a pair of shaped electrode plates 93,93' disposed symmetrically to either side of beam B and a pair of parallel grid electrodes 94,94' in the space between the shaped electrode plates.

The shaped electrode plates are in the form of hyperbolae

and, when energised to a suitable d.c. voltage, they generate a quadrupole bunching field, similar to that produced by ion buncher 90 in Figure 7. This bunching field is created by virtue of field penetration through the grid electrodes 94,94'.

In the "filling" mode, the shaped electrode plates 93,93' are energised causing ions to accumulate in beam section S, whereas the grid electrodes are maintained at earth potential. Then, in the "extraction" mode, the shaped electrode plates are de-energised and grid electrode 94 is pulsed to a d.c. voltage causing beam section S to be accelerated sideways, in the transverse (X-axis) direction. A suitable slit or aperture is provided in plate 93' allowing the beam section to exit the space between the shaped electrode plates.

It will be appreciated that, in general, the described arrangements employ either one of, or a combination of, two different techniques to achieve the desired focussing effect; namely, the use of one or more focussing element, such as an ion lens or ion mirror, and the use of means to modify the energy and distribution of ions in the beam section S.

CLAIMS

1. A time-of-flight mass spectrometer comprising,
an ion source,
beam-forming means for producing a beam of ions generated by the ion source, the beam of ions extending along a path,
an extraction means for accelerating a section of the beam transversely with respect to the direction of the path,
focussing means for bringing ions in the accelerated section of beam, having the same mass-to-charge ratio, to a focus with respect to both time and space, and
means for detecting the ions focussed by the focussing means.
2. A mass spectrometer as claimed in claim 1, wherein the focussing means is an ion mirror.
3. A mass spectrometer as claimed in claim 2, wherein the ion mirror comprises field-generating means for generating a non-uniform electrostatic reflecting field.
4. A mass spectrometer as claimed in claim 3, wherein the non-uniform electrostatic reflecting field is an electrostatic quadrupole field having two-dimensional

symmetry.

5. A mass spectrometer as claimed in claim 4, wherein the ion mirror comprises a monopole electrode structure operating at d.c. voltage.

6. A mass spectrometer as claimed in claim 5, wherein the monopole electrode structure comprises a first electrode having a curvilinear transverse cross-section and a second electrode having a substantially V-shaped transverse cross-section, the second electrode being maintained, in use, at a d.c. retarding voltage with respect to the first electrode whereby to generate said electrostatic quadrupole field between the electrodes, and the first electrode being of a form to enable ions in the accelerated section of beam to enter the electrostatic quadrupole field between the electrodes.

7. A mass spectrometer as claimed in claim 1, wherein the focussing means comprises an electrostatic lens for generating an accelerating field in the form of an electrostatic quadrupole field, or any non-linear field having symmetry about an axis which is substantially orthogonal to the direction of the beam path.

8. A mass spectrometer as claimed in claim 7, wherein

the electrostatic lens comprises a plurality of electrodes spaced at intervals along said axis, each said electrode corresponding to a respective equipotential in the electrostatic quadrupole field.

9. A mass spectrometer as claimed in claim 8, wherein the focussing means further includes a drift tube which is maintained in use at a d.c. voltage different from that at the downstream electrode of said plurality of electrodes.

10. A time-of-flight mass spectrometer comprising an ion source,

beam-forming means for producing a beam of ions generated by the ion source, the beam of ions extending along a path,

extraction means for accelerating a section of the beam transversely with respect to the direction of the beam path,

focussing means for focussing ions in the accelerated section of beam, which have the same mass-to-charge ratio, with respect to both time and space, and

means for detecting the ions focussed by the focussing means,

wherein the focussing means comprises modifying means for modifying the component of ion energy in the

direction of the beam path as a function of position along said section of beam prior to said section of beam being accelerated transversely with respect to the direction of the beam path.

11. A mass spectrometer as claimed in claim 10, wherein the modifying means comprises ion buncher means for accumulating ions in said section of beam prior to said section being accelerated transversely with respect to the direction of the beam path.

12. A mass spectrometer as claimed in claim 11, wherein the ion buncher means comprises field-generating means for generating a retarding field in the form of an electrostatic quadrupole field having symmetry about the direction of the beam path.

13. A mass spectrometer as claimed in claim 12, wherein the field-generating means of the ion buncher means comprises a plurality of electrodes spaced at intervals along the beam path, each electrode corresponding to a respective equipotential in the electrostatic quadrupole field.

14. A mass spectrometer as claimed in claim 12, wherein the extraction means includes means to generate a

transverse electrostatic accelerating field between respective parts of the buncher means disposed to either side of the beam path.

15. A mass spectrometer as claimed in any one of claims 10 to 14, wherein the focussing means further comprises an ion mirror.

16. A mass spectrometer as claimed in claim 15, wherein the ion mirror comprises field generating means for generating a non-uniform electrostatic reflecting field.

17. A mass spectrometer as claimed in claim 16, wherein the non-uniform electrostatic reflecting field is an electrostatic quadrupole field having two-dimensional symmetry about an axis which is orthogonal to the direction of the beam path.

18. A mass spectrometer as claimed in claim 17, wherein the ion mirror comprises a monopole electrode structure operating at a d.c. voltage.

19. A mass spectrometer as claimed in claim 18, wherein the monopole electrode structure comprises a first electrode having a curvilinear transverse cross-section, and a second electrode having a substantially V-shaped

transverse cross-section, the second electrode being maintained, in use, at a d.c. retarding voltage with respect to the first electrode whereby to generate said electrostatic quadrupole field between the electrodes, and the first electrode being of a form to enable ions in the accelerated section of beam to enter the electrostatic quadrupole field between the electrodes.

20. A mass spectrometer as claimed in any one of claims 10 to 12, wherein the ion buncher means comprises a pair of shaped, non-planar electrode plates disposed symmetrically to either side of the beam path.

21. A time-of-flight mass spectrometer comprising,
an ion source,

beam-forming means for producing a beam of ions generated by the ion source, the beam of ions extending along a path,

an extraction means for accelerating a section of the beam transversely with respect to the direction of the path,

focussing means for bringing ions in the accelerated section of beam, having the same mass-to-charge ratio, to a focus with respect to both time and space, and

means for detecting the ions focussed by the focussing means,

wherein the extraction means is effective to modify ion energy as a function of position along the beam path.

22. A mass spectrometer as claimed in claim 21, wherein the extraction means and the focussing means comprise, in combination, accelerating means to subject said section of beam to a transverse accelerating field whose strength and direction changes monotonically from one end of the beam to the opposite end thereof, and deflection means for subjecting the accelerated section of beam to an electrostatic deflection force which is substantially parallel to the direction of the beam path.

23. A mass spectrometer as claimed in claim 22, wherein the accelerating means comprises first and second electrode plates arranged to either side of the beam path, one of the plates being inclined relative to the other.

24. A mass spectrometer substantially as herein described with reference to the accompanying drawings.

(0664H)

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

GB 9300406.7

Relevant Technical fields

(i) UK Cl (Edition L) H1D - DMAA, DMC, DMD, DME,
DMF

(ii) Int Cl (Edition 5) H01J

Search Examiner

R H LITTLEMORE

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search

19 APRIL 1993

Documents considered relevant following a search in respect of claims 1-24

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
Y	GB 1448322	(UNIVERSITY OF ROCHESTER) See analyser shown in Figures 2 and 4	21, 22
X	GB 1326279	(BENDIX CORP) See Figures 1, 3, 8, 10, 12-15	1, 7-9
Y	EP 0456517 A2	(KRATOS ANALYTICAL) See Figures 3 and 8	2-6, 10-20
Y	EP 0456516 A2	(KRATOS ANALYTICAL) See Figure 3	2-6, 10-20
Y	EP 0408288 A1	(KRATOS ANALYTICAL) See Figures 5(a) and 5(b)	2-6 at least
X	WO 91/03071 A1	(INST EN PROB KHIUS ETC) See Figure 1 and abstract	1-3
X	WO 89/06044 A1	(UNISEARCH) See whole document	1, 7-9

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).